

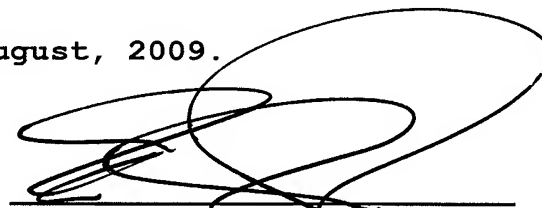
DECLARATION

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do hereby solemnly and sincerely declare:

- 1) THAT I am well acquainted with the Japanese language  
and English language, and
- 2) THAT the attached is a full, true, accurate and  
faithful translation into the English language made  
by me of Japanese Patent Application No. 2003-123274.

The undersigned declares further that all  
statements made herein of his own knowledge are true and  
that all statements made on information and belief are  
believed to be true; and further that these statements  
were made with the knowledge that willful false statements  
and the like so made are punishable by fine or imprisonment,  
or both, under section 1001, of Title 18 of the United  
States Code and that such willful false statements may  
jeopardize the validity of the application or any patent  
issuing thereon.

Signed this 10<sup>th</sup> day of August, 2009.



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2003-123274

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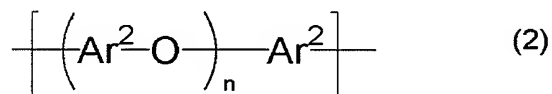
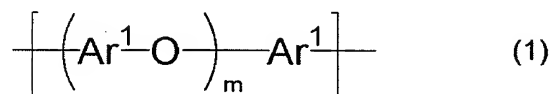
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[Kind of Document]      Description

[Title of the Invention]    AROMATIC-POLYETHER-TYPE ION-  
 CONDUCTIVE ULTRAHIGH MOLECULAR  
 WEIGHT POLYMER, INTERMEDIATE  
 5                            THEREFOR, AND PROCESSES FOR  
                              PRODUCING THESE

[Claims]

[Claim 1]    An aromatic-polyether-type ion-conductive  
 ultrahigh molecular weight polymer having an ion  
 10    exchange capacity of 0.1 meq/g or higher and a structure  
      comprising an aromatic-polyether-type ultrahigh  
      molecular weight polymer in which an acid group is  
      introduced, said aromatic-polyether-type ultrahigh  
      molecular weight polymer having at least one structural  
 15    unit selected from those represented by the following  
      formulas (1) and (2) and the sum of the number a of the  
      structural unit of the formula (1) and the number b of  
      the structural unit of the formula (2) being 2 or  
      larger:



20    (wherein Ar<sup>1</sup> and Ar<sup>2</sup> independently represent an aromatic  
      divalent group, m and n represent repeating numbers, m

and n independently represent a numeral of 10 or more,  
and a plurality of Ar<sup>1</sup>, a plurality of Ar<sup>2</sup>, a plurality  
of m and a plurality of n may be different  
respectively).

- 5 [Claim 2] An aromatic-polyether-type ion-conductive  
ultrahigh molecular weight polymer according to claim 1,  
wherein the acid group is sulfonic acid group.

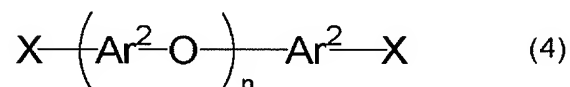
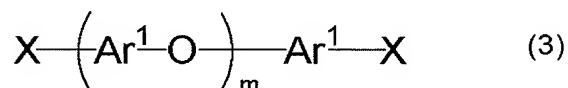
[Claim 3] A process for producing the aromatic-  
polyether-type ion-conductive ultrahigh molecular weight  
10 polymer of claim 1 which comprises introducing an acid  
group into an aromatic-polyether-type ultrahigh  
molecular weight polymer having at least one structural  
unit selected from those represented by the formulas (1)  
and (2) described in claim 1, the sum of the number a of  
15 the structural unit of the formula (1) and the number b  
of the structural unit of the formula (2) being 2 or  
larger.

[Claim 4] A process according to claim 3, wherein the  
acid group is sulfonic acid group.

- 20 [Claim 5] An aromatic-polyether-type ultrahigh  
molecular weight polymer having at least one structural  
unit selected from those represented by the formulas (1)  
and (2) described in claim 1, the sum of the number a of  
the structural unit of the formula (1) and the number b  
25 of the structural unit of the formula (2) being 2 or  
larger.

[Claim 6] A process for producing an aromatic-  
polyether-type ultrahigh molecular weight polymer of

claim 5 which comprises polymerizing by a condensation reaction at least one polymer selected from the polymers represented by the following formulas (3) and (4) in the presence of a zerovalent transition metal complex:



5 (wherein  $\text{Ar}^1$ ,  $\text{Ar}^2$ ,  $m$  and  $n$  are the same as defined above,  $X$  represents a group which is eliminated at the condensation reaction, and a plurality of  $X$  may be different).

[Claim 7] A process for producing an aromatic-  
10 polyether-type ultrahigh molecular weight polymer according to claim 6, wherein  $X$  is chlorine, bromine, iodine, *p*-toluenesulfonyloxy group, methanesulfonyloxy group or trifluoromethanesulfonyloxy group.

[Claim 8] A polymer electrolyte comprising the  
15 aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer of claim 1 as an effective component.

[Claim 9] A polymer electrolyte membrane comprising the polymer electrolyte of claim 8.

20 [Claim 10] A fuel cell comprising the polymer electrolyte membrane of claim 9

[Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to an aromatic-  
5 polyether-type ion-conductive ultrahigh molecular weight  
polymer, an intermediate therefor, a process for  
producing the same, and uses thereof.

[0002]

[Prior Art, Problem to be solved by the Invention]

Polymer electrolytes comprising polymers  
10 having ion-conductivity are used as diaphragms of  
electrochemical devices such as primary batteries,  
secondary batteries and solid polymer type fuel cells.  
For example, perfluorosulfonic acid-based materials such  
as Nafion (trademark of DuPont de Nemours, E.I., Co.)  
15 have been mainly used because they are superior in  
characteristics when used in fuel cells. However, these  
materials suffer from the problems that they are very  
expensive, low in heat resistance, and low in film  
strength, which requires some reinforcement for  
20 practical use.

[0003]

Under such circumstances, development of  
inexpensive polymers substitutable for the above ion-  
conductive polymers is now hastened. Among them, those  
25 which are promising are polymers comprising an aromatic  
polyether excellent in heat resistance and high in film  
strength into which an acid group such as sulfonic acid

group is introduced, namely, aromatic polymers having an aromatic main chain to which an acid group such as sulfonic acid group is directly bonded. For example, there are proposed aromatic-polyether-type ion-  
5 conductive polymers such as sulfonated polyether ketone type (Patent Document 1) and sulfonated polyether sulfone type (Patent Documents 2 and 3).

The film strength of these aromatic-polyether-type ion-conductive polymers is higher than that of  
10 perfluorosulfonic acid-based materials, but is not sufficiently satisfactory when they are used as electrolyte membranes of fuel cells and the like. Thus, development of electrolytes improved in this point has been desired.

15 [0004]

[Patent Document 1]: JP-A-11-502,249

[Patent Document 2]: JP-A-10-45,913

[Patent Document 3]: JP-A-10-21,943

[0005]

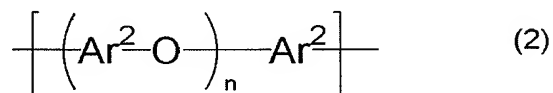
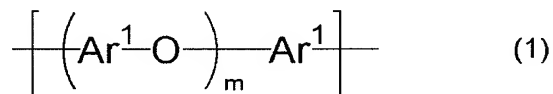
20 [Means for Solving the Problem]

As a result of intensive research conducted by the inventors in an attempt to provide aromatic-polyether-type ion-conductive polymers improved in mechanical strength, it has been found that the  
25 molecular weight of the aromatic-polyether-type polymers can be further increased by a condensation reaction utilizing the terminal group of the polymers, namely, by coupling aromatic-polyether-type polymers per se which

have halogen or the like as a terminal group, whereby aromatic polyethers of ultrahigh molecular weight can be obtained, and it has been further found that ion-conductive ultrahigh molecular weight polymers  
 5 comprising this aromatic-polyether-type ultrahigh molecular weight polymer in which a sulfonic acid group or the like introduced can be made to electrolyte membranes having excellent film strength. As a result of further various researches, the present invention has  
 10 been accomplished.

[0006]

That is, the present invention provides an aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer which has an ion exchange  
 15 capacity of 0.1 meq/g or higher and has a structure comprising an aromatic-polyether-type ultrahigh molecular weight polymer in which an acid group introduced, said aromatic-polyether-type ultrahigh molecular weight polymer having at least one structural  
 20 unit selected from the units represented by the following formulas (1) and (2) and the sum of the number a of the structural unit of the formula (1) and the number b of the structural unit of the formula (2) being 2 or larger:



(wherein  $Ar^1$  and  $Ar^2$  independently represent an aromatic divalent group, m and n represent a repeating number, m and n independently represent a numeral of 10 or more, and a plurality of  $Ar^1$ , a plurality of  $Ar^2$ , a plurality  
5 of m and a plurality of n may be different respectively), an intermediate therefor, a process for producing the same, and uses thereof.

[0007]

[Mode for Carrying Out the Invention]

10           The present invention will be explained in detail below.

          The ion exchange capacity of the aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer of the present invention is 0.1 meq/g or higher,  
15 preferably about 0.1-4 meq/g, more preferably about 0.8-2.5 meq/g. When the aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer is used as a polymer electrolyte for fuel cells, if the ion exchange capacity is too low, proton-conductivity is low  
20 and the function as an electrolyte is sometimes insufficient. If it is too high, water resistance may deteriorate, which is not preferred.

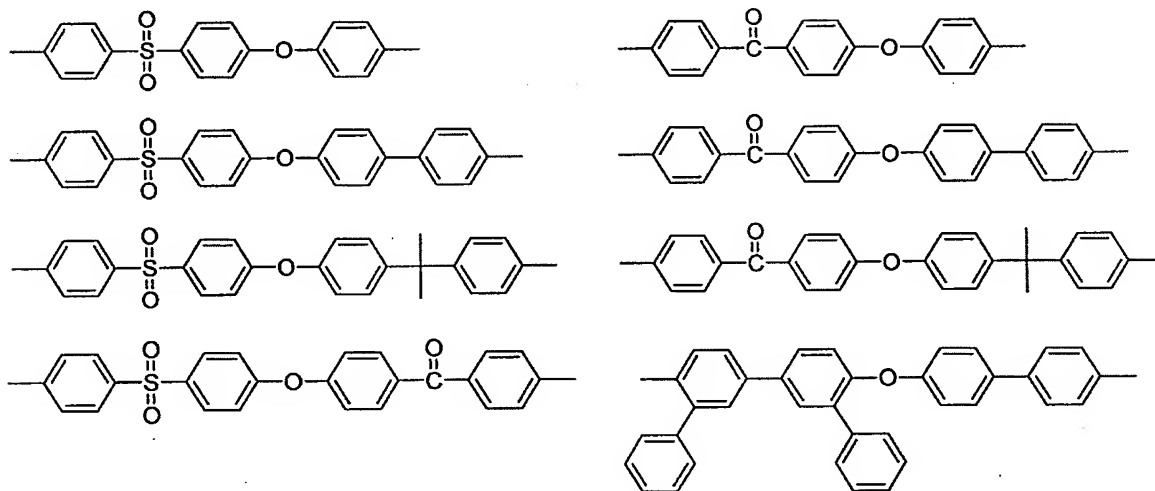
[0008]

          Furthermore, the aromatic-polyether-type ion-  
25 conductive ultrahigh molecular weight polymer of the present invention has a structure comprising an aromatic-polyether-type ultrahigh molecular weight polymer and an acid group introduced therein, and

contains at least one structural unit selected from those represented by the above-mentioned formulas (1) and (2) in which the sum of the number a of the structural unit represented by the formula (1) and the number b of the structural unit represented by the formula (2) is 2 or larger.

$Ar^1$  and  $Ar^2$  in the formulas (1) and (2) represent independently an aromatic divalent group, and typical examples of the aromatic divalent group are 1,4-phenylene, 1,3-phenylene, 1,2-phenylene, 2-phenyl-1,4-phenylene, 2-phenoxy-1,4-phenylene, 1,4-naphthylene, 2,3-naphthylene, 1,5-naphthylene, 2,6-naphthylene, 2,7-naphthylene, biphenyl-4,4'-diyl, biphenyl-3,3'-diyl, biphenyl-3,4'-diyl, 3,3'-diphenylbiphenyl-4,4'-diyl, 3,3'-diphenoxybiphenyl-4,4'-diyl, 2,2-diphenylpropane-4',4''-diyl, diphenylether-4,4'-diyl, diphenylsulfone-4,4'-diyl, benzophenone-4,4'-diyl, and divalent groups containing an ether linkage as shown below.

[0009]



These aromatic divalent groups may have substituents, and the substituents are preferably those which do not hinder the condensation reaction mentioned hereafter, such as, for example, an alkyl of 1-6 carbon  
5 atoms, an alkoxy of 1-6 carbon atoms, phenyl, and phenoxy. Especially preferred are methyl, ethyl, methoxy, ethoxy, phenyl and phenoxy. The position of the substituent is not particularly limited.

As aforementioned, a plurality of the  
10 respective  $Ar^1$  and  $Ar^2$  may be different.

[0010]

The symbols m and n which indicate the repeating number represent independently a numeral of 10 or more, preferably about 20-250, more preferably about  
15 50-200. A plurality of the respective m and n may be different as aforementioned.

The sum of the number a of the structural unit represented by the formula (1) and the number b of the structural unit represented by the formula (2) is 2 or  
20 larger, and preferably about 3-10.

Examples of the acid groups are carboxylic acid group, sulfonic acid group, sulfonylimide group, phosphonic acid group, etc. Sulfonic acid group and sulfonylimide group are preferred when the polymer is  
25 used as a polymer electrolyte of fuel cells and the like.

The number-average molecular weight in terms of polystyrene is usually about 2,000-100,000,

preferably about 5,000-80,000 for the structural units of the formula (1) and the formula (2), respectively, and is usually about 100,000 or more, preferably about 150,000 or more, more preferably about 200,000-400,000  
5 for the aromatic-polyether-type ultrahigh molecular weight polymer.

[0011]

The aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer of the present  
10 invention can have such a structure as comprising the above aromatic-polyether-type ultrahigh molecular weight polymer in which an acid group is introduced, and the process for producing it is not particularly limited. For example, it can be produced by introducing an acid  
15 group in the above aromatic-polyether-type ultrahigh molecular weight polymer.

The method for introduction of the acid group can be known one. For example, in the case of introducing a sulfonic acid group in the aromatic ring,  
20 there may be employed a method which comprises dispersing or dissolving the aromatic-polyether-type ultrahigh molecular weight polymer in concentrated sulfuric acid and, if necessary, heating or adding fuming sulfuric acid (e.g., Patent Documents 2 and 3,  
25 etc.).

In the case of introducing a carboxylic acid group, there may be used a method of brominating the aromatic-polyether-type ultrahigh molecular weight

polymer by a known method (e.g., JP-A-2002-241,493,  
Polymer, 1989, Vol. 30, June, 1137-1142, etc.) and  
thereafter introducing a carboxylic acid group by an  
action of carbon dioxide using the Grignard reaction, a  
5 method of introducing an acyl group or an alkyl group  
using a known method such as Friedel-Crafts reaction and  
thereafter converting the acyl group or alkyl group to a  
carboxylic acid group by a known oxidation reaction, and  
the like.

10 [0012]

In the case of introducing a sulfonylimide  
group, there may be used a method of converting the  
sulfonic acid group introduced, for example, by the  
above method to a sulfonyl halide group such as sulfonyl  
15 chloride by the action of thionyl chloride or the like,  
a method of introducing a sulfonyl chloride group by the  
action of chlorosulfuric acid into the aromatic-  
polyether-type ultrahigh molecular weight polymer, if  
necessary, in an organic solvent and then acting a  
20 sulfonylamide compound such as methanesulfonylamide or  
benzenesulfonylamide, if necessary, in the presence of a  
deoxidizer to introduce a sulfonylimide group, and other  
methods.

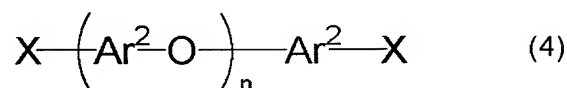
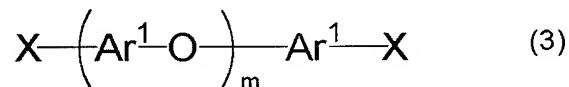
In the case of introducing a phosphonic acid  
25 group, there may be used a method of introducing a bromo  
group according to a known method, thereafter acting a  
trialkyl phosphite in the presence of a nickel compound  
such as nickel chloride to introduce a phosphonic acid

diester group, and hydrolyzing it by a known method  
 (e.g., Chem. Ber., 103, 2428-2436 (1970), etc.), a  
 method of forming a C-P linkage by Friedel-Crafts  
 reaction using phosphorus trichloride or phosphorus  
 5 pentachloride in the presence of a Lewis acid catalyst,  
 and, if necessary, carrying out oxidation and hydrolysis  
 to convert to a phosphonic acid group, a method of  
 acting phosphoric acid anhydride at high temperatures  
 (e.g., J. Amer. Chem. Soc., 76, 1045-1051 (1954), etc.),  
 10 and other methods.

[0013]

Next, the process for producing the aromatic-  
 polyether-type ultrahigh molecular weight polymer will  
 be explained.

15 The aromatic-polyether-type ultrahigh  
 molecular weight polymer can be produced by polymerizing  
 at least one polymer selected from the polymers  
 represented by the following formulas (3) and (4) in the  
 presence of a zerovalent transition metal complex by a  
 20 condensation reaction:



(wherein  $\text{Ar}^1$ ,  $\text{Ar}^2$ ,  $m$  and  $n$  are the same as defined  
 hereinbefore,  $X$  represents a group which is eliminated  
 at the condensation reaction, and a plurality of  $X$  may

be different).

[0014]

Here, X represents a group which is eliminated at the time of the condensation reaction. As the  
5 specific examples thereof, mention may be made of halogens such as chlorine, bromine and iodine, and sulfonic acid ester groups such as p-toluenesulfonyloxy group, methanesulfonyloxy group and trifluoromethanesulfonyloxy group.

10 [0015]

The polymerization by condensation reaction is carried out in the presence of a zerovalent transition metal complex, and examples of the zerovalent transition metal complex are zerovalent nickel complex, zerovalent  
15 palladium complex, etc. Among them, the zerovalent nickel complex is preferred.

The zerovalent palladium complexes include, for example, tetrakis(triphenylphosphine)palladium(0), etc.

20 Examples of the zerovalent nickel complexes include bis(cyclooctadiene)nickel(0), (ethylene)bis(triphenylphosphine)nickel(0), tetrakis(triphenylphosphine)nickel(0), etc. Among them, preferred is bis(cyclooctadiene)nickel(0).

25 The amount of the zerovalent transition metal complex is usually 0.1-5 times in mol, preferably about 1-3 times in mol with respect to the total mol number of the polymers represented by the formula (3) and the

formula (4).

[0016]

In the condensation reaction, it is preferred that a ligand is further present. The ligands include, 5 for example, nitrogen-containing ligands such as 2,2'-bipyridyl, 1,10-phenanthroline, methylenebisoxazoline and N,N,N',N'-tetramethylethylenediamine, tertiary phosphine ligands such as triphenylphosphine, tritolylphosphine, tributylphosphine and 10 triphenoxyphosphine, etc. Among them, 2,2'-bipyridyl is particularly preferred.

In case the ligand is allowed to coexist, ordinarily this is used in a molar ratio of about 0.2-2, preferably about 1-1.5 (on the basis of metal atom) with 15 respect to the zerovalent transition metal complex.

[0017]

The condensation reaction is usually carried out in the presence of a solvent. Examples of the solvent are aromatic hydrocarbon solvents such as 20 benzene, toluene, xylene and naphthalene; ether solvents such as diisopropyl ether, tetrahydrofuran, 1,4-dioxane and diphenyl ether; amide solvents such as N,N-dimethylformamide and N,N-dimethylacetamide. These may be used in admixture of two or more. Among them, 25 toluene, tetrahydrofuran, N,N-dimethylformamide, and mixtures of two or more of them are preferred.

The solvents are used in an amount of usually about 5-500 times in weight, preferably about 20-100

times in weight with respect to the monomers, namely,  
the above polymers.

The condensation temperature is usually about  
0-250°C, preferably about 10-100°C, and the condensation  
5 time is usually about 0.5-24 hours.

[0018]

The resulting aromatic-polyether-type  
ultrahigh molecular weight polymer is a simple re-  
extended polymer represented by, for example, the  
10 formula (3) as mentioned above when  $Ar^1$  and  $Ar^2$  in the  
formulas (3) and (4) are the same and is a block  
copolymer of a polymer represented by the formula (3)  
and a polymer represented by the formula (4) when they  
are different.

15 Usually, in a process for producing a  
condensation type block copolymer, in order to adjust  
the compositional ratio of each block, it is necessary  
to control the molecular weight of each block precursor  
polymer and accurately adjust the equivalent of the  
20 reactive terminal group, while according to the present  
invention, a block copolymer of preferred composition  
can be synthesized only by controlling the charging  
weight ratio.

[0019]

25 The aromatic-polyether-type ultrahigh  
molecular weight polymer produced by the condensation  
reaction can be separated from the reaction mixture by a  
conventional method. For example, a poor solvent is

added to precipitate the polymer, and the desired product can be separated by filtration or the like. Furthermore, if necessary, it can be purified by usual purification method such as washing with water or re-  
5 precipitation using good solvent and poor solvent.

The polymerization degree of the aromatic-polyether-type ultrahigh molecular weight polymer and analysis of the polymer structure can be carried out by usual means such as GPC measurement and NMR measurement.

10 [0020]

Thus, the aromatic-polyether-type ultrahigh molecular weight polymer is obtained. The polymerization degree of the polymer is shown by  $(m \times a + n \times b)$ , and according to the present invention, there  
15 can be produced polymers having very high molecular weight, for example, those having a polymerization degree of 500 or more, which cannot be produced by the conventional processes.

The number-average molecular weight in terms  
20 of polystyrene is usually about 100,000 or more, preferably about 150,000 or more, more preferably about 200,000-400,000.

[0021]

Next, explanation will be made of the case  
25 where the aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer of the present invention is used as a diaphragm of electrochemical devices such as fuel cells.

In this case, the polymer is used ordinarily in the form of a film, and the method of converting the polymer to a film is not particularly limited, and, for example, a method of forming a film from the polymer in the state of solution (solution casting method) is preferred.

Specifically, a copolymer is dissolved in a suitable solvent and the solution is cast coated on a support such as a glass plate, followed by removing the solvent to form a film. The solvent used for the film formation is not particularly limited so long as it can dissolve the copolymer and can be removed later. There may be suitably used, for example, non-protonic polar solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone and dimethylsulfoxide; chlorine-based solvents such as dichloromethane, chloroform, 1,2-dichloroethane, chlorobenzene and dichlorobenzene; alcohols such as methanol, ethanol and propanol; and alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether and propylene glycol monoethyl ether. If necessary, these may be used in admixture of two or more. Of these solvents, dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, etc. are preferred because solubility of the polymer in these solvents is high.

[0022]

The thickness of the film is not particularly limited, and is preferably 10-300  $\mu\text{m}$ , more preferably 15-100  $\text{m}\mu$ . If the thickness is less than 10  $\mu\text{m}$ , the  
5 film may not have sufficient practical strength, and if it is more than 300  $\mu\text{m}$ , the film is high in membrane resistance, which tends to deteriorate the characteristics of electrochemical devices. The film thickness can be controlled by the concentration of  
10 solution and the coating thickness on the support.

[0023]

Furthermore, for the purpose of improving various physical properties of the film, plasticizers, stabilizers, releasing agents, etc. which are used in  
15 the field of polymers can be added to the aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer of the present invention. Moreover, it is possible to compositely alloy the copolymer of the present invention with other polymers by a method of  
20 mixing in the same solvent and co-casting the mixture.

In the use for fuel cells, it is known to add an inorganic or organic fine particles as a water retaining agent for attaining easy water control. All of these known methods can be used so long as attainment  
25 of the object of the present invention is not hindered.

[0024]

Moreover, for the purpose of improving mechanical strength of the film, the polymer can be

crosslinked by irradiation with electron rays or radioactive rays. Furthermore, there is known a method of impregnating a porous film or sheet with the polymer to make a composite film or sheet or a method of  
5 reinforcing the film by mixing with a fiber or pulp, and all of these known methods can be used so long as attainment of the object of the present invention is not hindered.

[0025]

10               Next, the fuel cell of the present invention will be explained.

              The fuel cell of the present invention can be produced by bonding a catalyst and an electrically conductive material as a collector to both sides of a  
15 film comprising the aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer.  
Furthermore, the aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer of the present invention can also be used as an ion-conducting  
20 component of the catalyst layer. That is, the aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer of the present invention can be used as the electrolyte membrane of a polymer electrolyte membrane-electrode assembly used in fuel cells and as the ion-  
25 conducting component of the catalyst layer. A polymer electrolyte membrane-electrode assembly can also be obtained by using the ultrahigh molecular weight polymer as both the electrolyte membrane and the ion-conducting

component.

The catalyst is not particularly limited so long as it can activate the oxidation-reduction reaction with hydrogen or oxygen, and known catalysts can be  
5 used, and it is preferred to use fine particles of platinum or a platinum alloy. The fine particles of platinum supported on particulate or fibrous carbon such as active carbon or graphite are preferably used.

[0026]

10 For the electrically conductive materials as collectors, known materials can also be used, and porous carbon woven fabrics, carbon nonwoven fabrics or carbon papers are preferred since they efficiently transport a raw material gas to the catalyst.

15 The method for bonding platinum fine particles or platinum fine particles-supporting carbon to the porous carbon nonwoven fabric or carbon paper and the method for bonding them to the polymer electrolyte film are disclosed, for example, in J. Electrochem. Soc. :  
20 Electrochemical Science and Technology, 1988, 135(9), 2209, and these known methods can be used.

Thus produced fuel cell of the present invention can be used in various forms which use hydrogen gas, modified hydrogen gas or methanol as  
25 fuels.

[0027]

Examples

The present invention will be explained in

detail by the following examples, which should not be construed as limiting the invention in any manner.

The molecular weight in the examples is a number-average molecular weight (Mn) and a weight-average molecular weight (Mw) in terms of polystyrene measured by GPC.

Mechanical properties of the film are measured by the following methods.

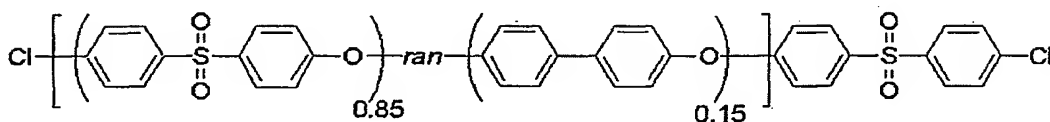
The aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer or the like is dissolved in DMAc and the concentration is adjusted to 10 wt%. Then, the solution is cast-coated on a glass support and the solvent is removed to prepare a film. Then, a test piece is punched out from the film by dumbbell cutter-1223 manufactured by Dumbbell Co., Ltd., and breaking elongation is measured at room temperature and 50% RH and at a testing rate of 10 mm/min.

[0028]

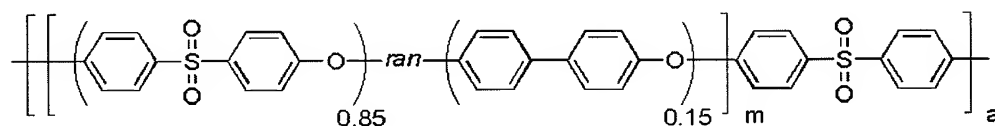
#### Example 1

<Production of aromatic-polyether-type ultrahigh molecular weight polymer a-1>

In argon atmosphere, 20 g of the following polyether sulfone copolymer (the suffixes 0.85 and 0.15 at the repeating units of the random copolymer show mol%):



(having  $M_n = 5.50 \times 10^4$  and prepared in accordance with the process disclosed in Example 3 of JP-A-10-21,943 and 0.468 g (3.00 mmol) of 2,2'-bipyridyl were dissolved in 800 mL of DMAc, the solution was subjected to bubbling  
 5 for 30 minutes with argon gas, and 0.824 g (3.00 mmol) of  $Ni(COD)_2$  was added thereto, followed by heating to  $80^\circ C$ , stirring with keeping at that temperature for 8 hours, and then leaving for cooling. Then, the reaction mixture was poured into 500 mL of 4N hydrochloric acid  
 10 and the resulting white precipitate was filtered off and purified by re-precipitation according to a usual method to obtain the following aromatic-polyether-type ultrahigh molecular weight polymer a-1. The ultrahigh molecular weight polymer was quantitatively recovered.  
 15 The molecular weight of the resulting ultrahigh molecular weight polymer was measured to obtain  $M_n = 2.20 \times 10^5$ ,  $M_w = 3.93 \times 10^5$  (GPC, polystyrene standard). The ultrahigh molecular weight polymer was a polymer which was extended about fourfold.



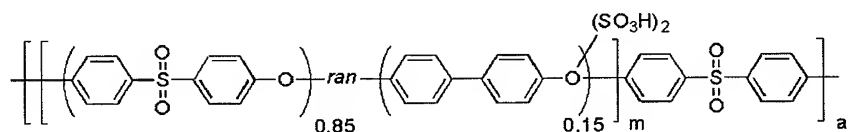
20 [0029]

## Example 2

<Production of aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer b-1>

10 g of the above aromatic-polyether-type

ultrahigh molecular weight polymer a-1 was dissolved in 80 g of concentrated sulfuric acid, and sulfonated at room temperature for 48 hours, followed by purification by a conventional method to obtain an aromatic-  
 5 polyether-type ion-conductive ultrahigh molecular weight polymer b-1 shown below. The resulting polymer had an ion exchange capacity of 1.15 meq/g. Furthermore, it had a breaking elongation of 25%.

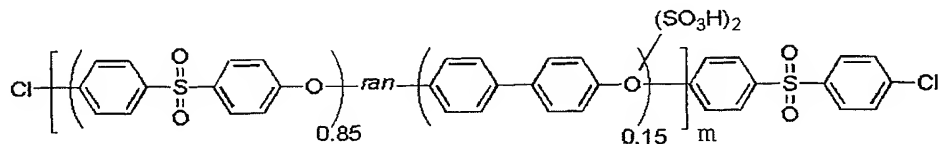


[0030]

#### Comparative Example 1

10 <Production of aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer b'-1>

An aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer b'-1 as shown below was obtained by carrying out the sulfonation and  
 15 purification in the same manner as in Example 2, except that 5 g of the same polyether sulfone copolymer as used in Example 1 was used in place of the aromatic-polyether-type ultrahigh molecular weight polymer 1. The resulting polymer had an ion exchange capacity of  
 20 1.10 meq/g. Furthermore, it had a breaking elongation of 7%.

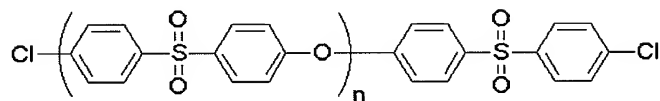


[0031]

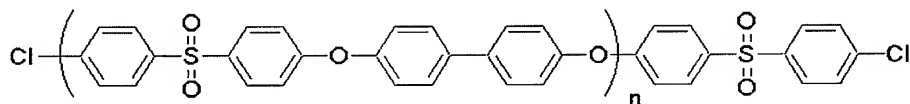
Example 3

<Production of aromatic-polyether-type  
ultrahigh molecular weight polymer a-2>

5 In argon atmosphere, 2.5 g of the following  
polyether sulfone of chloro-terminated type:

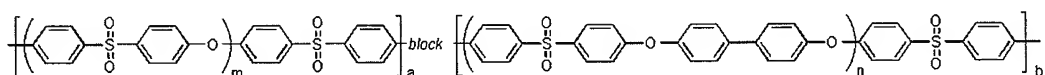


(SUMIKA EXCELL PES 5200P manufactured by Sumitomo  
Chemical Co., Ltd. and having  $\text{Mn} = 5.44 \times 10^4$  and  $\text{Mw} =$   
 $1.23 \times 10^5$ : GPC, polystyrene standard), 2.50 g of the  
10 following polyether sulfone copolymer:



(prepared in accordance with the process disclosed in  
Example 1 of JP-A-2002-220,469 and having  $\text{Mn} = 3.16 \times$   
 $10^4$  and  $\text{Mw} = 8.68 \times 10^4$ ) and 0.117 g (0.75 mmol) of  
2,2'-bipyridyl were dissolved in 200 mL of DMAc, the  
15 solution was subjected to bubbling with argon gas for 30  
minutes, and 0.206 g (0.75 mmol) of  $\text{Ni}(\text{COD})_2$  was added  
thereto, followed by heating to  $80^\circ\text{C}$ , stirring with  
keeping at that temperature for 6 hours, and then  
leaving for cooling. Then, the reaction mixture was  
20 poured into 500 mL of 4N hydrochloric acid and the

resulting white precipitate was filtered off and purified by re-precipitation according to a usual method to obtain the following aromatic-polyether-type ultrahigh molecular weight polymer a-2. The reaction  
 5 proceeded quantitatively. The molecular weight of the resulting ultrahigh molecular weight polymer was  $M_n = 1.89 \times 10^6$ ,  $M_w = 2.17 \times 10^6$  (GPC, polystyrene standard).

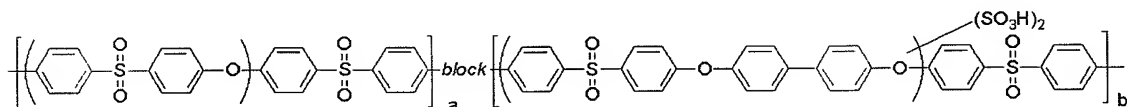


[0032]

#### Example 4

<Production of aromatic-polyether-type ion-  
 10 conductive ultrahigh molecular weight polymer b-2>

An aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer b-2 as shown below was obtained by carrying out the sulfonation and purification in the same manner as in Example 2, except  
 15 that 5 g of the aromatic-polyether-type ultrahigh molecular weight polymer a-2 was used. The resulting polymer had an ion exchange capacity of 1.77 meq/g.



[0033]

#### Example 5

<Production of aromatic-polyether-type

ultrahigh molecular weight polymer a-3>

In argon atmosphere, 5 g of the same polyether sulfone of chloro-terminated type as used in Example 3 (SUMIKA EXCELL PES 5200P manufactured by Sumitomo Chemical Co., Ltd.), 0.172 g (1.10 mmol) of 2,2'-bipyridyl and 15 ml of toluene were dissolved in 100 mL of DMSO, and water in the system was removed by distilling off toluene by heating at a bath temperature of 150°C. After leaving for cooling, 0.382 g (1.39 mmol) of Ni(COD)<sub>2</sub> was added thereto, followed by stirring with keeping at 60°C for 3 hours and at 80°C for 4 hours, and then leaving for cooling. The reaction mixture was poured into water, and the precipitate was washed with 10% hydrochloric acid and subsequently with water, and then dried.

The molecular weight of the resulting aromatic-polyether-type ultrahigh molecular weight polymer a-3 was measured to obtain  $M_n = 1.40 \times 10^5$ ,  $M_w = 3.33 \times 10^5$  (GPC, polystyrene standard). The ultrahigh molecular weight polymer was a polymer which was extended about threefold.

[0034]

[Advantages of the Invention]

According to the present invention, the molecular weight of an aromatic polyether can be further increased by a condensation reaction utilizing the terminal group of the polymer, namely, by coupling aromatic-polyether-type polymers per se which have

halogen or the like as a terminal group, and an aromatic polyether of ultrahigh molecular weight can be easily produced. Furthermore, an aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer obtained  
5 by introducing an acid group such as sulfonic acid group into the above aromatic-polyether-type ultrahigh molecular weight polymer can be made to an electrolyte membrane having excellent mechanical strength.

[Kind of Document] Abstract

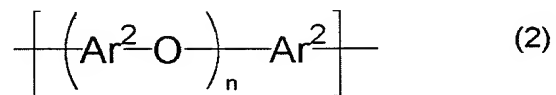
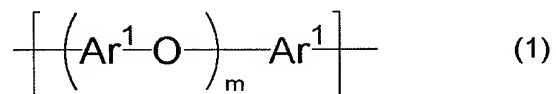
[Abstract]

[Problem]

An aromatic-polyether-type ion conductive polymer membrane having improved mechanical strength is provided.

[Solution]

An aromatic-polyether-type ion-conductive ultrahigh molecular weight polymer having an ion exchange capacity of 0.1 meq/g or higher and a structure comprising an aromatic-polyether-type ultrahigh molecular weight polymer in which an acid group is introduced, said aromatic-polyether-type ultrahigh molecular weight polymer having at least one structural unit selected from those represented by the following formulas (1) and (2) and the sum of the number a of the structural unit of the formula (1) and the number b of the structural unit of the formula (2) being 2 or larger:



[Selected Drawing] No